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PATENT SPECIFICATION

NO DRAWINGS

L148,550

Inventor: THOMAS ADAM CLAYTON

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COMPLETE SPECIFICATION

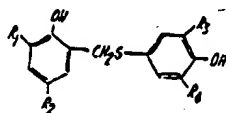
Substituted benzylphenyl sulfides and their
use as antioxidants

We, UNIROYAL INC., a corporation organised and existing under the laws of the State of New Jersey, one of the United States of America, of 1230 Avenue of the Americas, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with 2-hydroxy-3,5-dihydrocarbylbenzyl 3,5-dihydrocarbyl-4-hydroxyphenyl sulfides and process for their preparation.

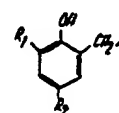
The compounds of the present invention display good antioxidant activity when utilized to prevent oxidative deterioration in various organic materials, e.g. rubber, plastics, fats and petroleum products.

The compounds of the present invention may be represented by the formula:

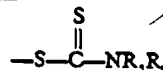


wherein R_1 , R_2 , R_3 and R_4 represent alkyl groups of 1 to 12 carbon atoms each, cycloalkyl groups of 6 to 8 carbon atoms each or aralkyl groups of 7 to 9 carbon atoms each. R_1 may also be hydrogen.

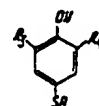
These compounds may be prepared by any convenient process. A preferred process of making the compounds comprises the reaction of (A) a compound of the general formula:



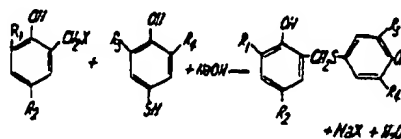
in which R_1 and R_2 are as defined above and X represents a benzothiazolyl sulfide radical, or an N,N-dialkylthiocarbamate group having the formula



in which R_1 and R_2 are lower alkyl groups (preferably having from 1 to 5 carbon atoms) with (B) a mercaptophenol of the formula:



in which R_3 and R_4 are as defined above under alkaline conditions according to the following equation:



[Price 4s. 6d.]

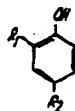
It is preferred to use equimolar amounts of the compound designated as A above, the mercaptophenol B and the alkali metal hydroxide, which is preferably sodium hydroxide.

5 The reaction is conveniently carried out in an aqueous reaction medium. The reaction medium preferably contains a water-miscible solvent such as a lower alkanol or ether such as methanol, ethanol, isopropanol, dioxane or ethylene glycol dimethyl ether. The reaction is preferably effected at a temperature from 10 room temperature to 100°C.

15 Preferred solvents for the reaction are methanol, ethanol and isopropanol. The preferred temperature is in the range of 50°C to 100°C, the reaction ordinarily being carried out at or near the reflux temperature of the solution. The preferred time of the reaction is up to four hours, although longer times may be used but are not necessary, the reaction 20 generally being complete in 30 minutes or less.

The reaction may also be carried out in a two-phase system such as benzene-water or xylene-water using vigorous agitation. Although longer reaction times are generally employed than in homogeneous solution, this heterogeneous system has the advantage of providing a simplified recovery procedure. In such a two-phase system, the product is soluble in the organic phase which can be readily separated from the aqueous phase containing the alkali metal dialkyldithiocarbamate or the alkali metal salt of 2-mercaptobenzothiazole. The product is then obtained by removing the solvent from the organic phase.

35 The intermediate 2 - hydroxy - 3,5 - dihydrocarbylbenzyl benzothiazolyl sulfides may be prepared by reacting one molar equivalent of a 2,4-dihydrocarbylphenol of the general formula:

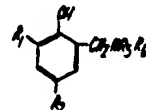


45 in which R₁ and R₂ are as defined above with one molar equivalent of formaldehyde and one molar equivalent of 2-mercaptobenzothiazole under acid conditions in a reaction similar to that described in U.S. patents 2,134,957 and 2,150,463.

50 The 2,4-dihydrocarbylphenols which may be used in the preparation of the intermediates include: 2,4-dimethylphenol; 2 - methyl - 4 - t - butylphenol; 2 - t - butyl - 4 - methylphenol; 2,4 - di - t - butylphenol; 2 - methyl - 4 - cyclohexylphenol; 2 - cyclohexyl - 4 - methylphenol; 2,4-dicyclohexylphenol; 2 - methyl - 4 - cyclooctylphenol; 2 - cyclooctyl - 55 4 - methylphenol; 2,4 - dicyclooctylphenol;

2 - methyl - 4 - t - octylphenol; 2 - t - octyl - 4 - methylphenol; 2,4 - di - t - octylphenol; 2 - nonyl - 4 - methylphenol; 2,4 - dinonylphenol; 2 - dodecyl - 4 - methylphenol; 2,4 - didodecylphenol; 2 - (alpha - methylbenzyl) - 4 - methylphenol; 2,4 - di(alpha - methylbenzyl)phenol; 2 - (alpha, alpha - dimethylbenzyl) - 4 - methylphenol; and 2,4 - di(alpha, alpha - dimethylbenzyl)phenol. 60 65

The intermediate 2 - hydroxy - 3,5 - dihydrocarbylbenzyl N,N - dialkyldithiocarbamates may be prepared by reacting a compound of the formula:



with carbon disulfide.

The mercaptophenols which may be used include: 2,6 - dimethyl - 4 - mercaptophenol; 2,6 - diisopropyl - 4 - mercaptophenol; 2 - methyl - 4 - mercapto - 6 - t - butylphenol; 2,6 - di - sec - butyl - 4 - mercaptophenol; 2,6 - di - t - butyl - 4 - mercaptophenol; 2 - methyl - 4 - mercapto - 6 - t - octylphenol; 2 - methyl - 4 - mercapto - 6 - cyclohexylphenol; 2,6 - dicyclooctyl - 4 - mercaptophenol; 2,6 - di(alpha-methylundecyl) - 4 - mercaptophenol; 2 - methyl - 4 - mercapto - 6 - (alpha - methylbenzyl)phenol; 2 - methyl - 4 - mercapto - 6 - (alpha, alpha - dimethylbenzyl)phenol; 2 - methyl - 4 - mercaptophenol; 2 - isopropyl - 4 - mercaptophenol; 2 - t - butyl - 4 - mercaptophenol; 2 - (alpha - methylundecyl) - 4 - mercaptophenol; 2 - cyclooctyl - 4 - mercaptophenol and 2 - (alpha - methylbenzyl) - 4 - mercaptophenol. 75 80 85 90

The invention will now be illustrated with reference to the following examples.

EXAMPLE 1

The preparation of 2 - hydroxy - 3 - t - butyl - 5 - methylbenzyl 3,5 - diisopropyl - 4 - hydroxyphenyl sulfide. 95

To a solution of 21 g. (0.1 mole) of 2,6 - diisopropyl - 4 - mercaptophenol and 8 g. (0.1 mole) of 50% aqueous sodium hydroxide in 150 ml. of ethanol was added 34.3 g. of 2 - hydroxy - 3 - t - butyl - 5 - methylbenzyl 2 - benzothiazolyl sulfide. The reaction mixture was refluxed gently for 20 minutes, cooled and poured into cold water. The product which separated was extracted with ether, dried with anhydrous sodium sulfate and evaporated down to a crystalline residue. The crystalline mass was broken up and washed with hexane yielding 32 g. (83%) of 2 - hydroxy - 3 - t - butyl - 5 - methylbenzyl 3,5 - diisopropyl - 100 105 110

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4 - hydroxyphenyl sulfide, m.p. 84—87°. Recrystallization from hexane raised the melting point to 88—89°.

Analysis:

5 Calc'd for $C_{21}H_{24}O_2S$:
%C, 74.61; %H, 8.81; %S, 8.29.
Found: %C, 74.56; %H, 9.02; %S, 8.08.

EXAMPLE 2

10 The preparation of 2 - hydroxy - 3 - (α - methylbenzyl) - 5 - methylbenzyl 3 - methyl - 4 - hydroxy - 5 - *t* - butylphenyl sulfide.

2 - Methyl - 4 - mercapto - 6 - *t* - butylphenol was reacted with 2 - hydroxy - 3 - (α - methylbenzyl) - 5 - methylbenzyl N,N - dimethyldithiocarbamate in the manner described in example 1 to yield 2 - hydroxy - 3 - (α - methylbenzyl) - 5 - methylbenzyl 3 - methyl - 4 - hydroxy - 5 - *t* - butylphenyl sulfide, m.p. 94—95° after recrystallization from hexane.

20 Analysis:

Calc'd for $C_{37}H_{48}O_2S$:
%C, 77.14; %H, 7.61; %S, 7.61.
Found: %C, 76.88; %H, 7.81; %S, 7.82.

EXAMPLE 3

25 The preparation of 2 - hydroxy - 3 - methyl - 5 - *t* - butylbenzyl 3 - methyl - 4 - hydroxy - *t* - butylphenyl sulfide.

2 - Methyl - 4 - mercapto - 6 - *t* - butylphenol was reacted with 2 - hydroxy - 3 - methyl - 5 - *t* - butylbenzyl N,N - dimethyldithiocarbamate in the manner described in example 1 to yield 2 - hydroxy - 3 - methyl - 5 - *t* - butylbenzyl 3 - methyl - 4 - hydroxy - 5 - *t* - butylphenyl sulfide, a very viscous oil:

35 Analysis:

Calc'd for $C_{23}H_{28}O_2S$:
%C, 74.20; %H, 8.60; %S, 8.60.
Found: %C, 74.39; %H, 8.67; %S, 8.39.

EXAMPLE 4

40 The preparation of 2 - hydroxy - 3 - *t* - butyl - 5 - methylbenzyl 3 - methyl - 4 - hydroxy - 5 - *t* - butylphenyl sulfide.

2 - Methyl - 4 - mercapto - 6 - *t* - butylphenol was reacted with 2 - hydroxy - 3 - *t* - butyl - 5 - methylbenzyl 2 - benzothiazolyl sulfide in the manner described in example 1 to yield 2 - hydroxy - 3 - *t* - butyl - 5 - methylbenzyl 3 - methyl - 4 - hydroxy - 5 - *t* - butylphenyl sulfide which was recrystallized from hexane, m.p. 93—95°, yield = 70%.

Analysis:

Calc'd for $C_{27}H_{32}O_2S$:
%C, 74.20; %H, 8.60; %S, 8.60.
Found: %C, 74.14; %H, 8.64; %S, 8.64.

EXAMPLE 5

55 The preparation of 2 - hydroxy - 3 - (1,1,3,3 - tetramethylbutyl) - 5 - methylbenzyl 3 - methyl - 4 - hydroxy - 5 - *t* - butylphenyl sulfide.

2 - Methyl - 4 - mercapto - 6 - *t* - butylphenol was reacted with 2 - hydroxy - 3 - (1,1,3,3 - tetramethylbutyl) - 5 - methylbenzyl 2 - benzothiazolyl sulfide in the manner described in example 1 to yield 2 - hydroxy - 3 - (1,1,3,3 - tetramethylbutyl) - 5 - methylbenzyl 3 - methyl - 4 - hydroxy - 5 - *t* - butylphenyl sulfide as a viscous oil.

EXAMPLE 6

70 The preparation of 2 - hydroxy - 3 - *t* - butyl - 5 - methylbenzyl 3 - methyl - 4 - hydroxy - 5 - *t* - butylphenyl sulfide in a two phase system.

In a 500 ml. 3-neck Morton flask was placed 19.6 g. (0.1 mole) of 2 - methyl - 4 - mercapto - 6 - *t* - butylphenol, 34.3 g. (0.1 mole) of 2 - hydroxy - 3 - *t* - butyl - 5 - methylbenzyl 2 - benzothiazolyl sulfide, 8.8 g. (0.11 mole) of 50% aqueous sodium hydroxide, 100 ml. of water and 100 ml. of benzene. The solution was stirred and heated at 70°C. for four hours. The mixture was then cooled and the benzene layer was separated. It was washed with water, dried with anhydrous sodium sulfate and evaporated down to a solid residue. The product was recrystallized from hexane to yield 31 g. (83%) of 2 - hydroxy - 3 - *t* - butyl - 5 - methylbenzyl 3 - methyl - 4 - hydroxy - 5 - *t* - butylphenyl sulfide, m.p. 92—95°.

EXAMPLE 7

90 The preparation of 2 - hydroxy - 3 - *t* - butyl - 5 - methylbenzyl 3 - methyl - 4 - hydroxyphenyl sulfide.

2 - Methyl - 4 - mercapto-phenol was reacted with 2 - hydroxy - 3 - *t* - butyl - 5 - methylbenzyl 2 - benzothiazolyl sulfide in the manner described in example 1 to yield 2 - hydroxy - 3 - *t* - butyl - 5 - methylbenzyl 3 - methyl - 4 - hydroxyphenyl sulfide as a viscous oil.

EXAMPLE 8

100 This example demonstrates the usefulness of a compound of this invention as an antioxidant for natural rubber.

A natural rubber composition was prepared in accordance with the following recipe:

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Masterbatch #1		Masterbatch #2	
Pale crepe	98.65	Pale crepe	90.0
Zinc oxide	10.00	Tetramethyl thiuram monosulfide	10.0
Lithopone	60.00		100.0
Finely divided CaCO ₃ (Whiting)	60.00		
Zinc laurate	0.50		
Sulfur	3.00		
Masterbatch #2	1.50		
	233.65		

The antioxidants (1 part) were then milled into 233.65 parts of masterbatch #1 and samples were cured at 274°F. for 20 minutes. 5 Tensile bars were aged in an oxygen bomb for 48 hours at 70°C. The percent retention of tensile strength after aging demonstrates the activity of the compounds as rubber anti-oxidants.

Compound		% Tensile retained
(1)	none	59
(2)	3-methyl-4-hydroxy-5-t-butylbenzyl 3-methyl-4-hydroxy-5-t-butylphenyl sulfide	73
(3)	2,2'-methylenebis(4-methyl-6-t-butylphenol)	84
(4)	2-hydroxy-3-(1,1,3,3-tetramethylbutyl)-5-methylbenzyl 3-methyl-4-hydroxy-5-t-butylphenyl sulfide	90

The results demonstrate the effectiveness of a compound of this invention (4) as an anti-oxidant and shows its advantage over a compound of the prior art (2) and a commercial bis-phenolic antioxidant (3). 15

The cured stocks were examined for discoloration and staining. In the results described below the rating is on a scale of 1 = very light to 10 = very dark where 0 represents no discoloration, y = yellow and r = tan. 20

Aging conditions	Compound (2)	Compound (3)	Compound (4)
15' NO ₂ fumes	4 y	3 r	3 y
2 weeks on roof	3 y	1 y	1 y
61 X Lacquer stain 8 hrs. sunlamp	off-white	off-white	0
61 K Lacquer stain 8 hrs. sunlamp	off-white	off-white	0

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5

These results demonstrate the advantage of a compound of this invention (4) in commercially important non-discoloring properties over a compound of the prior art (2).

EXAMPLE 9

This example demonstrates the usefulness of compounds of this invention as stabilizers for polyisoprene.

A commercial *cis*-polyisoprene synthetic rubber containing 2,6-di-*t*-butyl-*p*-cresol as a stabilizer was used as the base polymer. The polymer was dissolved in benzene so as to provide a 2% polymer solution. An aliquot portion of a benzene solution of the compound to be evaluated was added so as to provide 1% by weight of the additive based upon the weight of polymer in the solution. A thin film of rubber was then deposited on a sodium chloride disk by evaporating 10 drops of the

solution on the one-inch diameter disk.

The disks were then placed in a 130°C. oven and removed after 30 minutes, one hour and every hour thereafter. At each interval, the infrared spectrum of the polymer film was obtained. Oxidation of the polymer film is evidenced by the appearance of a band at 5.85 μ in the spectrum caused by the development of carbonyl groups in the polymer. The time of aging required for the appearance of this band in the spectrum is taken as the break time. The effectiveness of compounds as stabilizers can be evaluated by the length of time they protect the rubber against oxidation as determined by this carbonyl development test.

The use of infrared spectrophotometry in following the oxidation of polymer films has been described by Bishop [*Anal. Chem.*, 33, 456 (1961)].

Added Stabilizer	Hours to break
(1) None	1/2
(2) 3-Methyl-4-hydroxy-5- <i>t</i> -butylbenzyl 3-methyl-4-hydroxy-5- <i>t</i> -butylphenyl sulfide	4
(3) 2-Hydroxy-3- <i>t</i> -butyl-5-methylbenzyl 3-methyl- 4-hydroxy-5- <i>t</i> -butyl-phenyl sulfide	5

40 Non-discoloring characteristics were determined in this polymer by aging five grams of rubber contained from the above described

polymer solutions at 130°C. for one hour and observing for color formation.

Added Stabilizer	Color
(1) 3-methyl-4-hydroxy-5- <i>t</i> -butylbenzyl 3-methyl-4-hydroxy-5- <i>t</i> -butylphenyl sulfide	yellow
(2) 2-hydroxy-3- <i>t</i> -butyl-5-methylbenzyl 3-methyl-4-hydroxy-5- <i>t</i> -butylphenyl sulfide	colorless

The same type of evaluation was carried out on another set of compounds with the following results:

Added Stabilizer	Hours to break	Color
(1) 3,5-diisopropyl-4-hydroxy-benzyl 3-methyl-4-hydroxy-5- <i>t</i> -butyl- phenyl sulfide	3	yellow
(2) 2-hydroxy-3- <i>t</i> -butyl-5-methyl- benzyl 3,5-diisopropyl-4- hydroxyphenyl sulfide	3	colorless

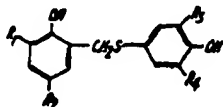
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These results show the significant advantage in non-discoloring properties of the compounds of this invention over the prior art compounds without loss in antioxidant activity.

WHAT WE CLAIM IS:—

1. A chemical compound of the formula:



(I)

wherein R_1 , R_2 , and R_3 represent alkyl groups having from 1 to 12 carbon atoms, cycloalkyl groups having from 6 to 8 carbon atoms or aralkyl groups having from 7 to 9 carbon atoms, and wherein R_4 represents an alkyl group having from 1 to 12 carbon atoms, a cycloalkyl group having from 6 to 8 carbon atoms, or an aralkyl group having from 7 to 9 carbon atoms, or hydrogen.

2. 2-hydroxy-3- τ -butyl-5-methylbenzyl 3,5-diisopropyl-4-hydroxyphenyl sulfide.

3. 2-hydroxy-3-(α -methylbenzyl)-5-methylbenzyl 3-methyl-4-hydroxy-5- τ -butylphenyl sulfide.

4. 2-hydroxy-3-methyl-5- τ -butylbenzyl 3-methyl-4-hydroxy-5- τ -butylphenyl sulfide.

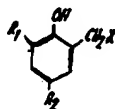
5. 2-hydroxy-3- τ -butyl-5-methylbenzyl 3-methyl-4-hydroxy-5- τ -butylphenyl sulfide.

6. 2-hydroxy-3-(1,1,3,3-tetramethylbutyl)-5-methylbenzyl 3-methyl-4-hydroxy-5- τ -butylphenyl sulfide.

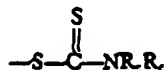
7. 2-hydroxy-3- τ -butyl-5-methylbenzyl 3-methyl-4-hydroxyphenyl sulfide.

8. Compounds as claimed in claim 1 specifically hereinbefore described.

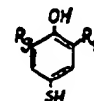
9. A method of preparing a compound represented by the formula: (I) given in claim 1 wherein R_1 , R_2 , R_3 , and R_4 have the meanings given in claim 1 which comprises reacting a compound of the formula



wherein R_1 and R_2 have the meanings given in claim 1 and X is a 2-benzothiazolyl group or an N,N-dialkylidithiocarbamate group of the formula



wherein R_2 and R_3 are lower alkyl groups, with a mercaptophenol of the formula



wherein R_2 and R_3 have the meanings given in claim 1, and an alkali metal hydroxide.

10. A process as claimed in claim 9 wherein the reaction is effected in an aqueous reaction medium.

11. A process as claimed in claim 9 or claim 10 wherein the reaction medium contains a water-miscible organic solvent.

12. A process as claimed in claim 11 wherein the organic solvent is a lower alcohol or an ether.

13. A process as claimed in claim 12 wherein the organic solvent is methanol, ethanol, isopropanol, dioxane or ethylene glycol dimethyl ether.

14. A process as claimed in claim 9 or claim 10 wherein the reaction is effected in a two-phase system.

15. A process as claimed in claim 14 wherein the two phase system is benzene-water or xylene-water.

16. A process as claimed in any one of claims 9 to 15 wherein the alkali metal hydroxide is sodium hydroxide.

17. A process as claimed in any one of claims 9 to 16 wherein equimolar amounts of mercaptophenol, dithiocarbamate and alkali metal hydroxide are employed.

18. A process as claimed in any one of claims 9 to 17 wherein the reaction is effected at a temperature of from ambient temperature to 100°C.

19. A process as claimed in claim 18 wherein the reaction is effected at a temperature of from 50°C. to 100°C.

20. A process as claimed in any one of the claims 9 to 19 wherein R_2 and R_3 contain from 1 to 5 carbon atoms each.

21. A process as claimed in claim 9 substantially as herein described.

22. A process as claimed in claim 9 substantially as herein described with reference to the foregoing Examples.

23. 3,5-dialkyl-2-hydroxybenzyl 3,5-dialkyl-4-hydroxyphenyl sulphides whenever prepared by a process as claimed in any one of claims 9 to 22.

24. A composition comprising an organic material normally subject to oxidative deterioration and a compound as claimed in any one of claims 1 to 3 as an anti-oxidant.

25. A composition as claimed in claim 24 wherein the said organic material is a plastic, fat or petroleum product.